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JAPANESE UNEXAMINED PATENT APPLICATION

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Applicant	Kao Soap Co. Ltd.

SPECIFICATION

1. TITLE

De-inking agent for recycling old paper.

2. CLAIM(S)

1. De-inking agent for recycling old paper, containing cellulase.

2. De-inking agent for recycling old paper, characterized by containing cellulase and surfactant.

3. De-inking agent for recycling old paper according to claim 2, containing cellulase and surfactant in a weight ratio of 1/500 - 2/5.

3. DETAILED DESCRIPTION OF THE INVENTION

This invention relates to a de-inking agent that can be used for recycling of old paper such as newspapers and magazines. More specifically, it relates to a de-inking agent that makes it possible to obtain a de-inked pulp of high whiteness and low residual ink number by the flotation method, rinsing method or combined flotation/rinsing method.

Recycle and reuse of old paper such as newspaper and magazines has long been practised; previously it was mostly used as an extender, but due to structural changes of raw material supply it has come to be considered as an important resource. Due to the development of de-inking techniques, it has become possible to obtain products of quality equivalent to virgin pulp. Particularly, de-inked newspaper pulp has now come to be used

instead of ground pulp. This is not only linked to the raw material situation, but also the energy cost is 1/5 - 1/8 of ground pulp or kraft pulp, sop it is effective for energy conservation. Further, de-inking of old paper can also be said to have great merit from the point of preservation of forest resources, and city waste disposal.

However, due to changes in printing techniques, printing methods and composition of printing ink, the adhesive force between paper and ink is nowadays stronger in old paper, so de-inking has become more difficult. Thus, while energy-conserving de-inking treatment for old paper has improved, it has become more difficult to remove the ink from the paper, and it has become very difficult to obtain recycled paper of high whiteness with the previously used cleaning agents.

Chemical substances previously known for use as de-inking agents for recycling of old paper are e.g. anionic surfactants such as alkyl-benzene sulphonate, alkyl sulphate, α-olefin sulphonate, dialkyl-sulpho-succinate and salts of higher fatty acids; non-ionic surfactants such as ethylene oxide adduct of higher alcohol, ethylene oxide adduct of alkyl-phenol, ethylene oxide adduct of fatty acid, ethylene oxide adduct of fatty acid amide, ethylene oxide adduct of polypropylene glycol, ethylene oxide adduct of fat and ethylene oxide/propylene oxide adduct (block or random) of higher alcohol; and amphoteric surfactants such as amine oxide. Further, it is also known to increase the effect by adding specified organic or inorganic builders and organic solvents together with these chemical substances. The de-inking efficiency by flotation and rinsing with these chemical substances and additives is not always high, and the demand for obtaining recycled paper of high whiteness cannot be satisfied.

As the result of efforts devoted to obtaining a de-inking agent having high de-inking efficiency in response to the demand for a technical innovation, the present inventors found that this objective can be met by using a de-inking for recycling of old paper which contains a certain enzyme, and they completed this invention.

Accordingly, this invention provides a de-inking agent for recycling old paper, containing cellulase.

Cellulase commonly occurring in plants, animals, bacteria and fungi can be used in this invention without any special restriction, but alkaline cellulase is especially preferred. Alkaline cellulase is one having optimum pH 8.0 - 11.5 (preferably 8.1 - 11.0).

Such enzyme retains its activity in the alkaline range as well as the acid and neutral range; e.g. a product purified and fractionated from cellulase culture liquid of various origins by salting out, precipitation, dialysis and gel filtration can be used, or crude enzyme or purified enzyme can be fractionated by electrophoresis or heat treated (e.g. 40-90°C for 0.5 min.-3 hrs.).

The following are examples of particularly preferred alkaline cellulases that can be used in the invention.

(1) Cellulase cultivated and recovered from *Bacillus sp.* with deposit Nos. FERM 1138, 1139, 1140 and 1141 (JP-B 50-28515).

(2) Cellulase originating from extract of midgut gland of *Dolabella auricula solander* (*Biochem. J. (1966) 99, 214-221*).

Additionally, examples of commercial products are No. 212 from Amano Pharmaceutical Co. and Cellulosin AP from Ueda Kagaku.

The invention decomposes the pulp slurry and achieves an excellent de-inking effect by reaction of the cellulase enzyme, and it shows even better de-inking effect by using this together with surfactant. Surfactant that can be used in the invention is one or more types selected from the group of non-ionic, anionic and amphoteric surfactants; specific examples are ethylene oxide adduct of higher alcohol, ethylene oxide adduct of alkyl-phenol, fatty acid amide of alkanol amine, ethylene oxide adduct of fatty acid amide, ethylene oxide adduct of fatty acid, ethylene oxide adduct of polypropylene glycol, polyethylene/polypropylene adduct of higher alcohol (block or random), ethylene oxide adduct of alkyl phosphate, alkyl betaine, α-olefin sulphonate, alkyl ether sulphate, alkyl sulphate, alkyl-benzene sulphonate and higher fatty acid. In this case, particularly excellent effect is achieved at a ratio of enzyme and surfactant (weight ratio) in the range 1/500 - 2/5.

Further, even better effect can be achieved by using it together with a builder such as sodium sulphate, sodium chloride, sodium silicate, sodium carbonate, calcium chloride, calcium carbonate, magnesium carbonate, sodium tripolyphosphate, sodium tri-meta-phosphate, sodium hexa-meta-phosphate, tri-sodium phosphate, sodium mono-hydrogen phosphate, sodium di-hydrogen phosphate, sodium pyrophosphate, sodium nitrilo-tri-acetic acid, carboxy-methyl cellulose or sodium gluconate.

The dosage of the cellulase-containing de-inking agent for old paper of the invention is sufficient above 0.002 weight-% cellulase relative to the raw material old paper.

Pulp of high whiteness can be obtained by adding the de-inking agent of the invention to the disintegration step or to the maturation tower.

In the practice of the invention, solvent, acid, alkali etc. can be added provided it does not impair the effect of the invention.

Below, the invention will be described by way of working examples, but the invention is not restricted to these examples.

Evaluation of the de-inking performance was done by measuring the whiteness of recycled pulp sheet in a comparative colorimeter (?). Further, it was also confirmed that the enzyme actually brought about a hydrolysis reaction by determining reducing sugar formed by the enzymatic hydrolysis as well as determining the L value of the drained liquid.

Example 1

Commercially recovered old newspaper, cut into 2 x 5 cm pieces, were fed into a laboratory disintegrator; inside this were added 1.0 % (relative to old paper) sodium hydroxide, 2.0 % (relative to old paper) sodium silicate, 1.0 % (relative to old paper) 30 % hydrogen peroxide and 0.3 % (relative to old paper) de-inking agent for recycling of old paper; after disintegration at 6 % pulp concentration, 45°C for 20 minutes, it was matured at 45°C for 1 hour. After concentrating to 15 % pulp concentration, it was diluted with water to 1 % concentration and made into a pulp sheet on a TAPPI sheet machine. When concentrating the pulp, the removed liquid was kept at 5°C for 12 hours, a fixed quantity of supernatant was recovered, and the L value was measured.

Results are shown in Table 1.

The enzyme used in this example was obtained by the method below.

Bacillus sp. nov. strain N4 (deposit No. FERM 1141) isolated from soil from Hirosawa, Wako-shi, Saitama-ken was inoculated into a medium (pH 10) containing 1.0 % peptone, 1.0 % meat extract, 1.0 % carboxymethyl cellulose (CMC), 0.5 % sodium

chloride, 0.1 % potassium dihydrogen phosphate, 1.0 % anhydrous sodium carbonate, and was cultivated with shaking at 37°C. After 72 hours cultivation, the cell mass was removed by centrifuging to obtain a crude enzyme, and this was dried with ethanol by conventional method to obtain cellulase powder. From 1 l culture liquid was obtained 10 g standard cellulase (enzyme activity at pH 6.0: 0.6 unit/mg solid) was obtained (hereinafter called cellulase N4).

Table 1.

No.		De-inking agent			De-inking effect	
		Surfactant [1] (a)	Enzyme (b)	Ratio (wt %) a / b	Pulp sheet whiteness (%)	Removed liquid L value (%)
This invention	1	$C_{12}C_{14}$ sec-alcohol EO_7	Cellulase M 4	95/5	46.7	32.8
	2	Nonyl-phenol EO_9		75/25	45.9	34.3
	3	$C_{12}C_{14}$ sec-alcohol EO_{12} PO_3		98/2	45.7	34.4
	4	Polypropylene glycol EO adduct (EO 20 %)		95/5	45.0	35.6
	5	Monoethanol amide EO_2		90/10	46.3	33.4
	6	Sodium dodecyl-benzene sulphonate		98/2	44.0	37.4
	7	α-olefin sulphonate (AOS_{124})		80/20	45.9	34.2
	8	Oleic acid soap		95/5	43.2	38.8
	9	Lauryl betaine		90/2	46.0	34.0
	10	-		-	43.6	38.0

No.		De-inking agent			De-inking effect	
		Surfactant [1] (a)	Enzyme (b)	Ratio (wt %) a / b	Pulp sheet whiteness (%)	Removed liquid L value (%)
Comparison	11	$C_{12}C_{14}$ sec-alcohol EO_7	--	--	43.2	38.3
	12	Nonyl-phenol EO_9			42.3	40.7
	13	$C_{12}C_{14}$ sec-alcohol EO_{12} PO_3			42.1	42.8
	14	Polypropylene glycol EO adduct (EO 20 %)			41.0	46.2
	15	Monoethanol amide ED_2			42.8	40.5
	16	Sodium dodecyl-benzene sulphonate			42.0	43.0
	17	α-olefin sulphonate (AOS_{124})			42.2	40.9
	18	Oleic acid soap			42.0	42.9
	19	Lauryl betaine			42.5	42.0
	20	-			40.3	49.9

1) EO: units of ethylene oxide, PO: units of propylene oxide, figures indicating mole numbers

Example 2

Commercial recovered old newspapers were cut in 2 x 5 cm pieces, a fixed amount was fed into a laboratory disintegrator, water and 1.0 % (relative to raw material old paper) sodium hydroxide were added, and disintegration was done at pulp concentration 5 %, 40°C for 20 minutes. After disintegration, 0.2 % de-inking agent (relative to raw material old paper) was added, and stirring was done at 45°C for 1 hour. It was then concentrated to 15 % pulp concentration, diluted to 1 % by adding water, and pulp sheet was made in a Buchner funnel. When the pulp was concentrated, the removed liquid was kept at 5°C for 12 hours, a fixed amount of supernatant was taken out and the L value was measured.

The results are shown in Table 2.

Table 2.

No.		De-inking agent			De-inking effect	
		Surfactant (a)	Enzyme (b)	Ratio (wt %) a / b	Pulp sheet whiteness (%)	Removed liquid L value (%)
This invention	21	$C_{12}C_{14}$ sec-alcohol EO_9	Cellulase N 4	99/1	42.7	39.6
	22	Diethanolamide (C_{12})		95/5	41.9	43.1
	23	2,4,7,9-tetramethyl-5-decin-4,7-diol EO_{10}		98/2	42.3	40.8
	24	2-ethyl-sesqui-phosphate EO_8		80/20	41.6	43.7
	25	Sodium lauryl sulphate		98/2	42.0	42.9
	26	--		-	40.3	50.0
Comparison	27	$C_{12}C_{14}$ sec-alcohol EO_8			39.9	50.7
	28	Diethanolamide (C_{12})			39.1	52.9
	29	2,4,7,9-tetramethyl-5-decin-4,7-diol EO_{10}			39.4	52.0
	30	2-ethyl-sesqui-phosphate EO_8			38.9	53.8
	31	Sodium lauryl sulphate			39.7	50.9
	32	--			38.5	54.7

Table 3.

	No.	De-inking agent				Whiteness (%)
		Surfactant (a)	Builder (b)	Enzyme (c)	Ratio (wt.%) (a)/(b)/(c)	
This invention	33	C_{12}-C_{14} sec-alcohol EO_{12}	$Na_5P_3O_{10}$	No. 212 cellulase (product of Amano Pharm.)	94/ 4/ 2	50.3
	34	Mono-ethanol amide EO_5			80/15/ 5	49.5
	35	Sodium dodecyl-benzene sulphonate	Na_2CO_3		90/ 8/ 2	48.9
	36	Sodium lauryl sulphate	Sodium nitrilo triacetate		95/2.5/2.5	48.1
	37	Stearyl-betaine			85/ 5/10	49.3
	38	C_{12}-C_{14} sec-alcohol EO_{12}	--	-"-	97.9/ 0/2.1	48.9
	39	Mono-ethanol amide EO_5			94.1/ 0/5.9	48.2
	40	Sodium dodecyl-benzene sulphonate			97.8/ 0/2.2	46.5
	41	Sodium lauryl sulphate			97.4/ 0/2.6	46.2
	42	Stearyl-betaine			89.5/ 0/10.5	48.3

Example 3

Commercial recovered old newspapers were cut in 2 x 5 cm pieces, a fixed amount was fed into a laboratory disintegrator, water and 1.0 % (relative to raw material old paper) sodium hydroxide, 2.5 % sodium silicate, 1 % of 30 % hydrogen peroxide and 0.2 % de-inking agent were added, and disintegration was done at 3 % pulp concentration, 40°C for 20 minutes, followed by maturation at 45°C for 90 minutes. Then the pulp concentration was diluted to 1 % by addition of water, and flotation treatment was done at 30°C for 10 minutes. The pulp slurry after the flotation treatment was concentrated to 6 % concentration and diluted to 1 % concentration by addition of water, and a pulp sheet was manufactured in a TAPPI machine.

The results are shown in Table 3.